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(54) Title: METHOD FOR DELIVERING CHEMICALS TO AN OIL OR GAS WELL

(57) Abstract: A method of delivering chemicals to well such as an oil or gas well, the method comprising encapsulating the chemicals in or on a carrier particle such as starch, and delivering the carrier-encapsulated chemical to the well.

WO 02/12674 A1

METHOD FOR DELIVERING CHEMICALS TO AN OIL OR GAS WELL

1
2
3 This invention relates to a method for encapsulating
4 chemicals and particularly to a method for starch
5 and wax encapsulation of aggressive chemicals for
6 applications in the oil industry. The invention
7 relates especially to a method of delivering
8 chemicals to an oil or gas well, in encapsulated
9 form.

10
11 Advances in drilling and completion technology have
12 revolutionized new field development and the use of
13 sub-sea wells with long tiebacks is now common. The
14 low temperatures and long fluid transport times
15 under sub-sea conditions often result in a wide
16 variety of production chemistry related problems,
17 including corrosion, scale, wax and asphaltene
18 deposition, hydrate formation, bacterial growth and
19 the transport of viscous fluids including emulsions.
20 The control of these problems is usually achieved by
21 continuous chemical injection at the sub-sea well
22 head along separate, multiple injection lines.

1 The installation of multiple chemical injection
2 lines is extremely expensive both for subsea
3 wellhead and continuous downhole injection,
4 especially in deepwater environments.

5
6 A deployment method which allowed a reduction in the
7 number of chemical injection lines required to
8 deliver the cocktail of chemicals required at each
9 wellhead would offer significant cost benefits.

10

11 The deployment of combined chemical treatment
12 packages, for example scale and corrosion
13 inhibitors, has been considered as one method of
14 reducing the number of chemical injection lines.
15 This has been achieved on a limited commercial basis
16 by blending selected oilfield chemicals together to
17 form a compatible mixture. However, the development
18 of combined chemical packages is fraught with
19 difficulties due to compatibility issues and is
20 limited to a small range of products and product
21 types. This limits the types of combined treatment
22 available and depending upon the nature of the
23 problem often still results in the use of several
24 injection lines.

25

26 According to the present invention there is provided
27 a method of delivering a chemical to an oil or gas
28 well, the method comprising associating the chemical
29 with a carrier, and delivering the chemical plus
30 carrier to the well.

31

1 The chemical can be encapsulated by the carrier or
2 otherwise entrapped by the carrier. The carrier
3 preferably comprises a suspension or slurry of
4 particles onto or into which the chemical can be
5 loaded. A typical carrier is particulate starch,
6 but other good carriers can be encapsulating agents
7 conventionally known from e.g. the food, paint and
8 pharmaceutical industries, such as gum arabic,
9 waxes, PVOH, polylactic acids, dextrans, low
10 viscosity modified starches, arabinogalactan, gum
11 acacia, casein, gelatin, carboxymethylcellulose,
12 tragacanth, karaya, sodium alginate, tannin, and
13 celluloses.

14
15 We have found that deploying the chemicals on or in
16 a slurry of nano/micro particles can alleviate
17 compatibility issues during storage and deployment
18 and thus facilitate the injection of multiple
19 chemicals via a single chemical injection line. The
20 nano/micro particles can typically contain a high
21 active level of oilfield chemical, typically 5-
22 90%v/v, and can be dispersed in either an aqueous or
23 oleic medium, and in solution or suspension,
24 depending upon the nature of the encapsulation
25 matrix. The entrapped oilfield chemicals are
26 typically released upon contact with the produced
27 fluids due to the breakdown of the coating or
28 carrier matrix either thermally and/or as a result
29 of mixing with oil or water. The potential to
30 control the rate and extent of release as a function
31 of time can also allow chemicals to be transported
32 and released along different sections of the

1 pipeline, thus alleviating some of the kinetic
2 problems associated with scale, wax and hydrate
3 inhibitors in long subsea tie backs.

4

5 This can enable the simultaneous delivery of
6 combined oilfield chemical packages to platform,
7 remote and complex wells through a single injection
8 line. The oilfield production chemical-entrapped
9 particles could be injected topsides, at sub sea
10 wellheads or elsewhere in the well. The particles
11 could also be applied to deliver oilfield chemicals
12 that cannot be effectively deployed by conventional
13 solvents. Certain embodiments may include the
14 delivery of a single oilfield chemical to a well
15 while associated with a carrier such as the above-
16 mentioned compounds.

17

18 The chemical is typically injected continuously into
19 the well, typically through a dedicated fluid line.

20

21 The nano/micro particle entrapment technology can be
22 applied to deliver a wide range and a wide
23 combination of oilfield production chemicals down
24 one injection line or umbilical. This includes, but
25 is not limited to scale inhibitors, corrosion
26 inhibitors, wax inhibitors, asphaltene inhibitors,
27 hydrate inhibitors, oxygen scavengers, hydrogen
28 sulphide scavengers, demulsifiers, biocides, gel
29 breakers, tracers, friction reducers, surfactants,
30 de-oilers and antifoaming agents. The oilfield
31 chemicals can be entrapped in either liquid or solid
32 form.

1 The particles can be manufactured using a variety of
2 techniques including complex coacervation,
3 interfacial polymerisation, desolvation, extrusion,
4 agglomeration, emulsion polymerisation, gelation,
5 chemical vapour deposition, fluid bed coating, spray
6 drying and combinations thereof. The particles can
7 be produced over a variable particle size,
8 typically, 1nm-850 μ m and can contain a high active
9 level of oilfield chemical, typically 1-90%v/v.
10 Nano/micro particles containing different oilfield
11 production chemicals can be dispersed into either an
12 aqueous or oleic carrier fluid, that may or may not
13 contain other oilfield production chemicals, using
14 either ionic or non-ionic surface active agents.
15 The material is preferably stable under injection
16 conditions in both aqueous and non-aqueous
17 environments at the ambient and sub-ambient
18 temperatures that may be encountered in a production
19 environment. The entrapped oilfield chemical can be
20 rapidly released from the encapsulating and/or
21 carrier medium as a result of either thermal
22 degradation of the matrix and/or dissolution in
23 either the oil or water phase, releasing the
24 oilfield chemical under wellhead conditions. The
25 release time of the chemical upon contact with the
26 produced fluids could also be delayed depending upon
27 the nature of the entrapment matrix. This can
28 allow chemicals to be transported and released along
29 different sections of the pipeline, thus enabling
30 the release of chemicals in the right place and
31 alleviating some of the kinetic problems associated

1 with scale, wax and hydrate inhibitors in long sub
2 sea tie backs.

3

4 The entrapment of certain oilfield chemicals could
5 reduce the corrosivity of the fluid to be deployed
6 into the wellhead or downhole injection system.

7 This could permit the umbilicals and downhole
8 injection lines to be fabricated from lower cost
9 carbon steels rather than the more expensive
10 stainless steels and/or corrosion resistant alloys.

11

12 The particles containing different production
13 chemicals, in either solid or liquid form, can then
14 be mixed together to produce the required blend of
15 oilfield chemicals for dispersion into the fluid
16 carrying medium which may be aqueous or organic
17 based. The solid particles could be dispersed into
18 the fluid-carrying medium by use of a wide range of
19 different types of amphoteric, anionic, cationic and
20 nonionic surface-active agents. Amphoteric
21 surfactants could include acetates such as lauro-,
22 alkyl- and coco-amphoacetates, betaines such as
23 lauryl-, alkyl- and coco-amidopropylbetaines,
24 glycines, imidazolines and propionates such as
25 lauro-, alkyl- and coco-aminodipropionate. Anionic
26 surfactants could include alkyl- alkylaryl-,
27 alkylether and alkylarylether sulphonates and
28 carbonates, lignin derivatives, olefine and paraffin
29 sulphonates, phosphate esters and sarcosinates.
30 Cationic surfactants could include amides, amines,
31 amidoamines, diamines and quaternaries such as
32 didecyldimethylammonium. Nonionic surfactants could

1 include alkoxylates such as alcohol-, alkylphenol-,
2 amide-, ester-, fatty acid- and glyceride
3 ethoxylates, alkylamides, amine oxides and esters.
4

5 The required dispersing characteristics could be
6 achieved for example by varying the ratio of a
7 sorbitan ester and a sorbitan ester ethoxylate to
8 achieve the desired hydrophilic - lipophilic balance
9 (HLB).
10

11 The chemical is typically coated or otherwise
12 associated with a carrier such as starch, flour or
13 wax. The starch can decompose at a given
14 temperature releasing the chemical at a second
15 location where it is needed. Selection of the
16 characteristics of the carrier (e.g. starch) used
17 allows accurate control over the temperature of
18 decomposition. Normally the temperature at the
19 wellhead will be hotter than the surface of the
20 well. The precise temperature at the wellhead will
21 vary from well to well, and typical subsea wellheads
22 may have an ambient temperature of around 110°C
23 (compared with 20°C at surface). The starch or wax
24 coat can typically be designed to decompose when it
25 crosses a point on the temperature gradient and so
26 release the chemicals. In particular, wax carriers
27 can be designed to degrade or dissolve slowly or
28 after a set time has elapsed to release the
29 chemicals continuously over a period of time or
30 after a set interval e.g. in the production fluids.
31 The starch or wax may be modified to decompose at
32 different temperatures as may be necessary for

1 particularly shallow or particularly deep wells or
2 for any other reason in which the temperature of the
3 wellhead may be different from normal. The starch
4 is typically granular starch, and resistant starch
5 made therefrom. The chemical is typically adsorbed
6 onto the starch, typically by simple mixing.
7 Adjuncts useful in controlled release formulations
8 can be added.

9

10 All granular starches and flours (hereinafter
11 "starch") may be suitable for use herein and may be
12 derived from any native source. A native starch as
13 used herein, is one as it is found in nature. Also
14 suitable are starches derived from a plant obtained
15 by standard breeding techniques including
16 crossbreeding, translocation, inversion,
17 transformation or any other method of gene or
18 chromosome engineering to include variations
19 thereof. In addition, starch derived from a plant
20 grown from artificial mutations and variations of
21 the above genetic composition, which may be produced
22 by known standard methods of mutation breeding, are
23 also suitable herein.

24

25 Typical sources for the starches are cereals,
26 tubers, roots, legumes and fruits. The native
27 source can be corn, pea, potato, sweet potato,
28 banana, barley, wheat, rice, sago, amaranth,
29 tapioca, arrowroot, canna, sorghum, and waxy or high
30 amylose varieties thereof. As used herein, the term
31 "waxy" is intended to include a starch containing at
32 least about 95% by weight amylopectin and the term

1 "high amylose" is intended to include a starch
2 containing at least about 40% by weight amylose.

3
4 Conversion products which retain their granular
5 structure may be derived from any of the starches,
6 including fluidity or thin-boiling starches prepared
7 by oxidation, enzyme conversion, acid hydrolysis,
8 heat and or acid dextrinization, and or sheared
9 products may also be useful herein.

10
11 Particularly useful are granular structures, which
12 have been "pitted" by the action of enzymes or acid,
13 leaving a still organised structure that creates a
14 microporous starch. The enzymatic or acid hydrolysis
15 of the starch granule is carried out using techniques
16 well known in the art. The amount of enzyme used is
17 dependent upon the enzyme, i.e., type, source and
18 activity, as well as enzyme concentration, substrate
19 concentration, pH, temperature, the presence or
20 absence of inhibitors, and the degree and type of
21 modification. Types of modifications are described
22 herein, *infra*. These parameters may be adjusted to
23 optimise the nature and extent of the "pitting" of
24 the starch granule.

25
26 Another particulate starch useful in the controlled
27 release applications of the present invention is
28 resistant starch. Resistant starch is commonly
29 known as a starch not likely to be adsorbed in the
30 small intestine of a healthy individual. Granular
31 or particulate starches, such as of the RS2-type (a
32 starch granule that resists digestion by pancreatic

1 alpha-amylase) and the RS4-type (a chemically
2 modified starch, such as acetylated,
3 hydroxyalkylated, or cross-linked starch) are
4 particularly suitable. However, resistant starches
5 of the RS3-type (retrograded, non-granular starch
6 formed by heat/moisture treatment of starch) are
7 also suitable for the instant invention due to their
8 high level of retrogradation or crystallisation from
9 the alignment and association of associated amylose.

10

11 These types of resistant starch are well known in
12 the art and may be exemplified by that disclosed in
13 US Patent Nos. US 5,593,503 which describes a method
14 of making a granular resistant starch; US Patent
15 Nos. 5,281,276 and 5,409,542 which describe methods
16 of making resistant starches of the RS3 type; US
17 5,855,946 which describes a method of making a
18 resistant starch of the RS4-type; and U.S.
19 Application Serial No. 60/157370, which describes
20 the formation of a very highly resistant starch.
21 The methods for making the resistant starches are
22 described in the preceding references, the
23 disclosures of which are incorporated herein by
24 reference.

25

26 The starch particulate, including granular and
27 resistant starches, may be modified by treatment
28 with any reagent or combination of reagents that
29 contribute to the controlled release properties of
30 the starch.

31

1 Chemical modifications are intended to include
2 crosslinked starches, including crosslinking the
3 particulate starch with reactive polymers.
4 Preferred reactive polymers include starches
5 modified with aldehyde or silanol groups. Other
6 chemical modifications include, without limit,
7 acetylated and organically esterified starches,
8 hydroxyethylated and hydroxypropylated starches,
9 phosphorylated and inorganically esterified
10 starches, cationic, anionic, non-ionic, and
11 zwitterionic starches, and succinate and substituted
12 succinate derivatives of starch.

13
14 Preferred modified starches are starch acetates
15 having a degree of substitution ("DS") of about up
16 to about 1.5, particularly those disclosed in US
17 5,321,132, thereby improving compatibility with
18 synthetic hydrophobic materials. Such
19 modifications are known in the art, for example in
20 Modified Starches: Properties and Uses, Ed.
21 Wurzburg, CRC Press, Inc., Florida (1986).

22
23 Other suitable modifications and methods for
24 producing particulate starches are known in the art
25 and disclosed in U.S. Patent No. 4,626,288 which is
26 incorporated herein by reference. In a particularly
27 useful embodiment, the starch is derivatized by
28 reaction with an alkenyl cyclic dicarboxylic acid
29 anhydride by the method disclosed in U.S. Patent
30 Nos. 2,613,206 and 2,661,349, incorporated herein by
31 reference, or propylene oxide, more particularly by
32 reaction with octenylsuccinic anhydride.

1 The encapsulated chemicals can be carried in a
2 liquid-phase inhibitor or other chemical to be
3 delivered to the well that may be incompatible with
4 the encapsulated chemical. All chemicals to be
5 delivered could then be injected through a single
6 umbilical. Two umbilicals could be installed to
7 allow operations to continue in the event of one
8 blocking up. Additionally a third umbilical for
9 methanol could be provided. A total of three
10 umbilicals could therefore provide adequate cover
11 for a well. This represents a significant saving
12 when compared with the prior art, which requires
13 five or six umbilicals for comparable performance.

14

15 Embodiments of the present invention will now be
16 described by way of example with reference to the
17 following examples.

18

19 **Example 1: Encapsulation of solid material**

20 US Patent 4755397 to Eden et al (incorporated herein
21 by reference) describes a process for the starch
22 encapsulation of a solid material, namely, ferric
23 hydroxide, which can be adapted for the
24 encapsulation of oilfield chemicals as follows.

25

26 The desired oilfield chemical is dissolved in
27 acidified water, dilute sodium hydroxide is added as
28 necessary while stirring to remove from the chemical
29 any trace precipitates. Ammonium sulphate, water and
30 high amylose (70%) cornstarch is added to the
31 chemical slurry to give a slurry of the following
32 composition:

| | | | |
|---|-------------------|------------|---------|
| 1 | Starch | 410 grams | (19.9%) |
| 2 | Ammonium sulphate | 610 grams | (29.6%) |
| 3 | Chemical | 41 grams | (2.0%) |
| 4 | Water | 1000 grams | (48.5%) |

5 This slurry is processed through a jet cooker (Model
6 C-1, National Starch & Chemical Corp) at 150°C. At
7 this temperature the high amylose starch cooks,
8 despite the presence of a high level of an
9 inhibiting salt, and forms a uniform dispersion. A
10 ball valve attached to the outlet of the jet cooker
11 can be adjusted so that a pressure drop from maximum
12 cooking temperature and pressure to atmospheric
13 pressure occurs as the starch cook passes through
14 the valve. Upstream the pressure is typically
15 90psig; downstream the pressure is typically 0psig.

16
17 As the starch passes through the valve and the
18 pressure is reduced to atmospheric, its temperature
19 drops to around 104°C, the boiling point of the salt
20 solution at atmospheric pressure. At this
21 temperature, the starch precipitates essentially
22 instantaneously entrapping the solid oilfield
23 chemical. The product collected at the cooker
24 outlet is typically a slurry of tan particles 5 to 7
25 microns in diameter. The slurry, by volume, is a
26 third salt solution and two thirds precipitated
27 particles. This product is washed free of salt and
28 dried.

29
30 The dried particles (40% by weight) containing the
31 various oilfield chemicals are then mixed with a
32 synthetic white oil such as Isopar M (52% by weight)

1 and a polyalkoxylated alkyl phenol based dispersant
2 (5% by weight) using a high shear, UltraTurrax mixer
3 at 5000 rpm for 10 minutes. A clay based thickening
4 agent (3% by weight) is then added to this mix and
5 blended using a high shear, UltraTurrax mixer at
6 10,000 rpm.

7
8 This process can be used for the production of
9 encapsulated particles containing a) solid biocides;
10 b) de-oilers; c) demulsifiers; d) scale inhibitors;
11 e) corrosion inhibitors; f) wax inhibitors; and
12 g) asphaltene inhibitors. The chemical-loaded
13 particles are mixed in various combinations of
14 chemicals and delivered through a single fluid
15 delivery pipeline to a wellhead, where the
16 temperature of around 110°C breaks down the starch
17 particles and releases the chemicals. Optionally a
18 liquid chemical such as a corrosion inhibitor is
19 mixed with the carrier fluid conveying the particles
20 to the well.

21
22 **Example 2: Encapsulation of an Active Ingredient**
23 WO9901214 to Fester et al (incorporated herein by
24 reference) describes a process for the encapsulation
25 of an active ingredient, namely, solids and water-
26 soluble fluids. This can be adapted for
27 encapsulation of oilfield chemicals as follows.

28
29 Fifteen grams of PN (native potato starch) are added
30 to 100ml water in which 2.5 g Tween 80 is dissolved.
31 Four grams TSTP are dissolved in this suspension,
32 followed by the addition of 20 g of salad oil. An

1 emulsion forms with the aid of an Ultra-Turrax.
2 The o/w emulsion is then emulsified in a second
3 hydrophobic phase, namely 200ml of paraffin oil. A
4 top stirrer at a speed of 600 rpm is used for this
5 purpose.

6
7 A solution of 0.65g NaOH in 10ml water is
8 subsequently added to the emulsion with stirring, in
9 order to initiate partial gelation and cross-
10 linking. After 30 minutes, the stirrer speed is
11 increased to 1000 rpm. After 4 hours the emulsion is
12 broken by addition of acetic acid.

13
14 The starch particles collected in the water/acetic
15 acid phase. After separation, the particles are
16 washed with de-ionised water and stored.
17 Examination of the dispersed fluid by light
18 microscopy should indicate that the particles are
19 essentially mono dispersed with a size of 25 μm
20 containing droplets of oil.

21
22 This process can be used for the production of
23 encapsulated particles containing solid and/or
24 liquid chemicals, namely, scale and corrosion
25 inhibitors, oxygen and hydrogen sulphide scavengers,
26 demulsifiers, gel breakers, tracers and antifoaming
27 agents. However, the process could be applicable to
28 any solid or water-soluble chemicals. As before the
29 particulate- entrapped chemicals are mixed in
30 various combinations of chemicals and delivered
31 through a single fluid delivery pipeline to a
32 wellhead, where the temperature of around 110°C

1 breaks down the starch particles and releases the
2 chemicals. Again the liquid phase of the carrier
3 fluid can incorporate a further chemical to be
4 delivered to the well.
5

6 **Example 3: Encapsulation of a Water Insoluble Liquid**

7 US Patent 4755397 to Eden et al (incorporated herein
8 by reference) describes a process for the starch
9 encapsulation of a water insoluble liquid, namely,
10 peppermint oil, and this can be adapted for the
11 production of starch encapsulation of hydrophobic
12 oilfield chemicals as follows.
13

14 A slurry is made of the following composition:

| | |
|-----------------------------------|-----|
| 15 High Amylose (70% Corn Starch) | 20% |
| 16 Ammonium Sulphate | 40% |
| 17 Water | 40% |

18

19 The following is mixed, to disperse the hydrophobic
20 oilfield chemical and added, with mixing, to the
21 previous slurry:
22

| | |
|----------------------|--------|
| 23 Oilfield chemical | 2-10% |
| 24 Surfactants | 90-98% |

25

26 The resulting slurry/coarse emulsion is jet-cooked
27 through a C-1 cooker as in Example 1. In this case,
28 the cooker outlet hose empties below the surface of
29 a slurry of ammonium sulphate and ice in saturated
30 ammonium sulphate solution (-8°C.) to condense and
31 trap any free peppermint oil vapours. The resulting
32 product is typically coarse (<20 mesh) light tan

1 powder in salt solution. The powder is recovered by
2 filtration and dried.

3
4 A 3% weight aqueous solution of HEC is then prepared
5 by slowly adding the powdered HEC to distilled water
6 and gradually increasing the mixing speed over a
7 five-minute period. Once a solution is formed a
8 sorbitan ester ethoxylate based dispersant (6% by
9 weight) is added to the aqueous HEC mixture and
10 blended at 2000rpm for five minutes. The dried
11 particles (50% by weight) containing the various
12 oilfield chemicals are then mixed with the aqueous
13 solution of HEC and dispersant using a high shear,
14 UltraTurrax mixer at 5000 rpm for 10 minutes.

15
16 This process is particularly useful for
17 manufacturing encapsulated products containing oil
18 soluble scale and corrosion inhibitors, wax and
19 asphaltene inhibitors, drag reducers, demulsifiers
20 and de-oilers. A variety of these chemicals can be
21 encapsulated as described above and delivered to a
22 wellhead via a single injection line in various
23 combinations, without interaction between the
24 chemicals in the line during delivery. Upon arrival
25 at the wellhead the starch capsules surrounding the
26 chemicals are broken down by the ambient temperature
27 at the wellhead, and the chemicals are released and
28 activated in situ. Incorporation of incompatible
29 liquid phase chemicals in the carrier fluid does not
30 affect the encapsulated chemical.

31

1 **Example 4: Encapsulation of a solid or oil soluble**
2 **product.**

3 US Patent 4997659 to Yatka et al (incorporated
4 herein by reference) describes a process for the
5 encapsulation of a powdered sweetener, namely,
6 Alitame in paraffin and/or microcrystalline wax.
7 This was adapted for the encapsulation of various
8 solid oilfield chemicals as listed above.

9
10 A 20% paraffin or micro-crystalline wax, of defined
11 melting point/80% solid oilfield chemical is
12 prepared by mixing the molten wax with the solid
13 chemical, cooling to form an agglomerate and
14 grinding up the agglomerate to form granules. These
15 granules are optionally further processed to form
16 spheres, using a spheroniser. The size of the
17 spheres is controlled by the granulation process but
18 is typically 1-50 μ m in diameter.

19
20 This process is typically used to produce paraffin
21 or microcrystalline wax-based particles containing
22 solid oilfield production chemicals such as scale,
23 wax and corrosion inhibitors, biocides and other
24 scavengers. In addition the wax particles can be
25 manufactured to entrap oil-based liquids such as
26 corrosion, wax and asphaltene inhibitors,
27 demulsifiers and de-oilers.

28
29 The nano/micro particles containing different
30 production chemicals, in either solid or liquid
31 form, are dispersed together to produce the required
32 blend of oilfield chemicals for dispersion into the

1 fluid carrying medium which was either aqueous or
2 organic based. The solid particles are dispersed
3 into the fluid-carrying medium by use of a wide
4 range of different dispersants. Suitable
5 dispersants include fatty acid esters and
6 alkoxyated (e.g. methoxyated or ethoxyated) fatty
7 acid esters such as sorbitan ester and sorbitan
8 ester ethoxylate; and PEG esters such as PEG
9 laurate. By varying the ratio of the ethoxyated
10 sorbitan ester to the sorbitan ester the desired HLB
11 can be obtained.

12
13 The encapsulated oil field chemicals are mixed in
14 the desired proportions and delivered via a single
15 fluid delivery line to a wellhead, at which point
16 the wax capsules degrade, releasing the chemical
17 into the wellhead environment. Optionally the two
18 or more chemicals that are delivered to the well can
19 be encapsulated by different methods e.g. according
20 to any of the examples herein, so that the different
21 particles release their chemical burdens at
22 different points in the well, in response to
23 different stimuli.

24
25 **Example 5: Encapsulation of a wax inhibitor by**
26 **starch.**

27 A granular starch (150g, starch octenylsuccinate,
28 aluminum salt, commercially available from National
29 Starch and Chemical Company) was added to a wax
30 inhibitor XPC 3147C (50 g, Aldrich) which had been
31 melted at a temperature greater than 30°C. The
32 mixture was stirred at ambient temperature and

1 pressure in a high shear disperser (Torrence,
2 #785049) at 2000-4000 rpm. An additional 100 g of
3 the granular starch was added to the mixture and
4 stirred for two more minutes to form a fine, free-
5 flowing powder. This is conveyed to a wellhead as
6 previously described through a single fluid line by
7 a carrier fluid that incorporates a scale inhibitor
8 that is incompatible with the wax inhibitor, without
9 any reaction between the chemicals. The scale
10 inhibitor treats the fluid conduit continuously from
11 the point of entry to the wellhead, and the wax
12 inhibitor is activated only after a longer period of
13 time as a result of the starch encapsulating matrix
14 dissolving in the produced fluids.

15

16 **Example 6: Encapsulation of a water-soluble chemical**
17 **by starch.**

18 Water-soluble solids were formulated with starch at
19 a 1:1 ratio (50% loading on starch). The oil well
20 chemical was solubilised in ambient water and
21 homogenised for 1-2 minutes at 9000-10000 rpm
22 (Silverson L4RT). The starch was then added to the
23 solution and the mixture was further homogenised for
24 2-3 minutes at 9000-10000rpm, 20°C (Silverson L4RT).
25 The mixture was spray dried (40% solids, 375°F inlet
26 temperature, 225°F outlet temperature with a feed
27 rate of 160ml/minutes and dual wheel atomisation
28 using Bowen Lab Model (30" x 36") to produce a
29 flowable, non-sticky composition.

30

31 a. The example was carried out using a scale
32 inhibitor, Scaletreat 2001-28, as the oil well

- 1 chemical and Vulca 90, a maize starch
2 crosslinked with 1.5% epichlorohydrin on dry
3 starch.
- 4 b. The example was carried out using a corrosion
5 inhibitor, Corrtreat 2001-29 as the oil well
6 chemical and a starch acetate (1.5 DS) waxy
7 maize starch.
- 8 c. The example was carried out using a scale
9 inhibitor, Scaletreat 2001-26 as the oil well
10 chemical and a microporous waxy maize starch
11 that was digested using 0.3% glucoamylase on
12 dry starch to achieve 15% digestion.

13

14 In each case, the encapsulated chemicals are mixed
15 as desired and delivered in mixtures of encapsulated
16 particles to the well-head through a single fluid
17 line. The encapsulated particles are degraded by
18 the fluid conditions at the well-head, and/or by
19 temperature, thereby delivering their active
20 reagents at the required position in the wellhead.

21

22 **Example 7: Encapsulation of a water insoluble**
23 **chemical by starch.**

24 Water insoluble solids were formulated with starch
25 at a 1:1 ratio (50% loading on starch). The oil
26 well chemical was added to a waxy maize starch
27 modified with 3% octenyl succinic anhydride and
28 converted to a water fluidity of 40, and the mixture
29 was homogenised for 1-2 minutes at 9000-10000 rpm,
30 20°C (Silverson L4RT). Water was added to the
31 emulsion and the mixture was further homogenised, 1
32 minute at 9000-10000 rpm, 20°C (Silverson L4RT).

1 The starch was then added to the solution and the
2 mixture was further homogenised, 1-2 minutes at
3 9000-10000 rpm, 20°C (Silverston L4RT). The mixture
4 was spray dried (35% solids, 380°F inlet
5 temperature, 230°F outlet temperature, 140-
6 160ml/minutes with dual wheel atomisation using
7 Bowen Lab Model (30" x 36")) to produce a flowable,
8 non-sticky composition.

9

- 10 a. The example was carried out using a wax
11 inhibitor, Waxtreat 398 as the oil well chemical
12 and a microporous waxy maize which was 30%
13 digested with 0.3% glucoamylase, and modified
14 with 3% octenyl succinic anhydride and
15 crosslinked with 1% aluminium sulphate.
- 16 b. The example was carried out using an asphaltene
17 dispersant, Waxtreat 7302 as the oil well
18 chemical and a microporous waxy maize starch
19 modified using 3% octenyl succinic anhydride,
20 enzymatically treated using 0.3% glucoamylase, to
21 achieve 30% digestion.
- 22 c. The example was carried out using a hydrogen
23 sulphide scavenger, Scavtreat 1020 as the oil
24 well chemical and a high amylose corn starch,
25 HYLON® VII starch, commercially available from
26 National Starch and Chemical Company.
- 27 d. The example was carried out using a kinetic
28 hydrate inhibitor, Hytreat 569 as the oil well
29 chemical and a microporous (30% enzyme digested)
30 waxy maize starch modified using 3% octenyl
31 succinic anhydride, enzymatically treated using
32 0.3% glucoamylase.

1 e. The example was carried out using an anti-
2 agglomerate hydrate inhibitor, Hytreat A560 as
3 the oil well chemical and a cationic starch
4 silanol, 0.3% Nitrogen, 0.4% silanol.

5
6 Chemicals are delivered through a single delivery
7 line to a wellhead and also to a well bore and
8 formation. The wellhead chemicals are released from
9 their encapsulated particles at the prevailing
10 wellhead conditions and the formation chemicals are
11 only released upon reaching the more aggressive
12 prevailing conditions at the formation.

13

14 **Example 8**

15 Starch was weighed out into a glass container. The
16 oil well chemical was added while mixing for 5
17 minutes and then mixed for an additional 5 minutes,
18 or until uniform using a Powerstat, Variable
19 Autotransformer set at 80 (3PN168), Bodine Electric
20 Co, Speed reducer motor (NSE-12R).

21

22 a. Starch used was a 50:50 blend of sago and
23 tapioca, DD and the oil well chemical used was
24 Waxtreat 398. The starch:chemical ratio used was
25 100:40 and the loading was 28.6%.

26 b. Starch used was a high amylose (70%) maize starch
27 modified by 3% octenyl succinic anhydride and 10%
28 polyvinyl alcohol and the oil well chemical used
29 was Waxtreat 398. The starch:chemical ratio used
30 was 100:80 and the loading was 44.4%.

31 c. Starch used was enzyme converted (alpha amylase)
32 maltodextrin and the oil well chemical used was

1 Trosquat. The starch:chemical ratio used was
2 100:38 and the loading was 27.5%.

3 d. Starch used was enzyme converted (alpha amylase)
4 maltodextrin and the oil well chemical used was
5 Trosquat. The starch:chemical ratio used was
6 100:38 and the loading was 27.5%.
7 e. Starch used was a high amylose (70%) maize that
8 was gelatinised, completely enzymatically de-
9 branched and retrograded and the oil well
10 chemical used was Hytreat A560. The
11 starch:chemical ratio used was 100:24 and the
12 loading was 19.3%.

13

14 The encapsulated chemicals are mixed as desired and
15 delivered to production tubing or other well
16 tubulars through a single fluid line. Once reaching
17 the target in the well the chemicals are released
18 through reaction to local conditions.

19

20 The wellhead is the preferred target of the
21 chemicals delivered in order to protect the tie
22 backs etc from corrosion or blockage, but it will be
23 appreciated that the present invention is not in any
24 way limited to the delivery of chemicals to the
25 wellhead, and in certain embodiments the delivery
26 target is another portion of the well, such as the
27 formation, the reservoir, the casing, production
28 tubing or other tubular or conduit.

29

30 Typical embodiments of the invention mitigate
31 compatibility problems with delivery of mixtures of
32 chemicals to platforms, remote and complex wells

1 through a single injection line. Some embodiments
2 also facilitate the deployment of certain chemicals
3 that are difficult to handle, for example, because
4 they are very corrosive and/or are insoluble in
5 conventional solvents; for example, polyacrylate wax
6 inhibitors, either alone or in combination with
7 other chemicals, where the chemicals or at least one
8 of them cannot be effectively deployed by
9 conventional solvents.

10

11 Certain embodiments also enable the deployment of
12 oilfield chemicals at high active concentrations,
13 for example, ethylene vinyl acetate (EVA) wax
14 inhibitors that cannot be effectively deployed at
15 >10%v/v by conventional solvents.

16

17 While starch is a preferred entrapping or coating
18 medium a range of other materials could be used such
19 as natural gums, cellulose and derivatives,
20 polysaccharides, gelatin, wax, fatty acids, acrylic,
21 carboxyvinyl polymers, polyester, polystyrene,
22 polycaprolactone, polyvinyl acetate, polyamides,
23 polyvinyl alcohol, polylactic acid, polyglycolide,
24 shellac, zein, oil based gels, silica gel and other
25 materials consisting of mixtures, copolymers,
26 terpolymers and hydrophobically and/or
27 hydrophilically modified and cross-linked
28 derivatives of the above.

29

30 In certain embodiments the nano/micro particles can
31 be dispersed in an aqueous or oleic medium depending
32 upon the encapsulation matrix, and can contain one

- 1 or more soluble or dispersed oilfield production
- 2 chemicals.
- 3
- 4 Modifications and improvements can be incorporated
- 5 without departing from the scope of the invention.

1 Claims

2 1. A method of delivering a chemical to an oil or
3 gas well, the method comprising associating the
4 chemical with a carrier, and delivering the
5 chemical and carrier to the well.

6

7 2. A method as claimed in claim 1, wherein the
8 chemical is encapsulated by the carrier.

9

10 3. A method as claimed in any preceding claim,
11 wherein the chemicals are released from the
12 carrier upon contact with the produced fluids
13 in the well.

14

15 4. A method as claimed in any preceding claim,
16 wherein two or more chemicals are delivered via
17 a single chemical injection conduit.

18

19 5. A method as claimed in claim 4, wherein the two
20 chemicals are mutually incompatible.

21

22 6. A method as claimed in claim 4 or claim 5,
23 wherein the two or more chemicals are released
24 from the carrier at different locations in the
25 well.

26

27 7. A method as claimed in any preceding claim,
28 wherein the or each chemical is aggressive,
29 insoluble or corrosive.

30

1 8. A method as claimed in any preceding claim,
2 wherein the chemical and carrier are carried by
3 a fluid to the desired point of delivery.

4
5 9. A method as claimed in claim 8, wherein the
6 fluid phase carries a further chemical to be
7 delivered to the well.

8
9 10. A method as claimed in claim 8 or claim 9,
10 wherein the fluid is aqueous fluid.

11
12 11. A method as claimed in claim 8, or claim 9
13 wherein the fluid is oleic or organic fluid.

14
15 12. A method as claimed in any preceding claim,
16 wherein the chemical-bearing carrier is
17 injected at surface.

18
19 13. A method as claimed in any preceding claim,
20 wherein the chemical-bearing carrier is
21 injected at a wellhead.

22
23 14. A method as claimed in any preceding claim,
24 wherein the chemical is selected from the group
25 comprising scale inhibitors, corrosion
26 inhibitors, wax inhibitors and dispersants,
27 asphaltene inhibitors and dispersants, hydrate
28 inhibitors, oxygen scavengers, pour-point
29 modifiers, hydrogen sulphide scavengers,
30 demulsifiers, biocides, gel breakers, tracers,
31 friction reducers, surfactants, de-oilers and
32 antifoaming agents.

- 1 15. A method as claimed in any preceding claim,
2 wherein the carrier is associated with the
3 chemical by a technique selected from the group
4 comprising coacervation, interfacial
5 polymerisation, desolvation, extrusion,
6 agglomeration, emulsion polymerisation,
7 gelation, chemical vapour deposition, fluid bed
8 coating, spray drying and combinations thereof.
9
- 10 16. A method as claimed in any preceding claim,
11 wherein the carrier is selected from the group
12 comprising starch or flour, gum arabic, waxes,
13 PVOH, polylactic acids, dextrans, low viscosity
14 modified starches, arabinogalactan, gum acacia,
15 casein, gelatin, carboxymethylcellulose,
16 tragacanth, karaya, sodium alginate, tannin,
17 and celluloses.
18
- 19 17. A method as claimed in any preceding claim,
20 wherein the chemical is continuously delivered
21 to the well.
22
- 23 18. A method as claimed in any preceding claim,
24 wherein the carrier and chemical forms a
25 particle.
26
- 27 19. A method as claimed in claim 18, wherein the
28 particle size is in the range of 1 μ m-20 μ m.
29
- 30 20. A method as claimed in any preceding claim,
31 wherein the carrier dissolves into the produced

- 1 fluids from the well after releasing the
- 2 chemical.

INTERNATIONAL SEARCH REPORT

Inten I Application No
PCT/GB 01/03547

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 E21B37/06 E21B43/25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-------------------------------------|
| X | US 4 611 664 A (OSTERHOUDT III M GLENN ET AL) 16 September 1986 (1986-09-16) column 2, line 35 -column 3, line 13; claims 1,2,5-9,12-16 column 4, line 21 - line 49 | 1-3,13, 14 |
| X | US 4 986 354 A (CANTU LISA A ET AL) 22 January 1991 (1991-01-22) column 1, line 38 -column 4, line 2 -/-- | 1-3,8, 10-12, 14,15, 17-20 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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|------------|---|-------------------------------------|
| X | WO 93 22537 A (PROCTER & GAMBLE) 11 November 1993 (1993-11-11) page 1, line 1 - line 30 page 4, line 31 -page 5, line 25 page 9, line 35 -page 11, line 15 page 16, line 11 - line 33; claims 1,5,6 ----- | 1-5,8, 10,11, 14-18,20 |
| X | US 4 986 353 A (CLARK CHARLES R ET AL) 22 January 1991 (1991-01-22) column 1, line 37 -column 4, line 19 ----- | 1-3,8, 10-12, 14,15, 17-20 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/GB 01/03547

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|--|
| US 4611664 | A | 16-09-1986 | NONE |
| US 4986354 | A | 22-01-1991 | NONE |
| WO 9322537 | A | 11-11-1993 | US 5922652 A 13-07-1999 AT 149237 T 15-03-1997 AU 4227493 A 29-11-1993 BR 9306321 A 26-03-1996 CA 2134980 A1 11-11-1993 CZ 9402703 A3 14-06-1995 DE 69308297 D1 03-04-1997 EP 0639240 A1 22-02-1995 FI 945196 A 04-11-1994 HU 70884 A2 28-11-1995 JP 7506408 T 13-07-1995 NO 944206 A 04-11-1994 NZ 252502 A 29-01-1997 RU 2111049 C1 20-05-1998 SK 132294 A3 11-07-1995 WO 9322537 A1 11-11-1993 |
| US 4986353 | A | 22-01-1991 | NONE |